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SYNTHESIS OF STAR POLY(4-VINYLPYRIDINE) ARCHITECTURE BY NITROXIDE MEDIATED POLYMERISATION

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Abstract

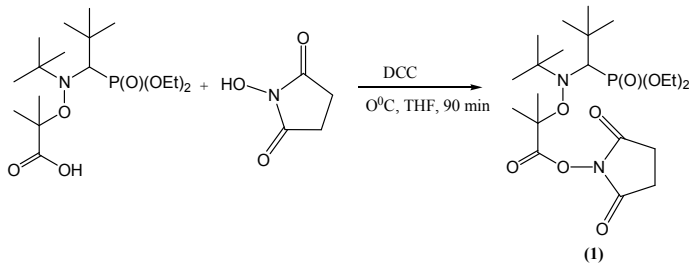
This study proposed multifunctional alkoxyamine 2-({tert-butyl [[1-(diethoxyphosphoryl)-2,2-dimethylpropyl]amino}oxy)-2-methylpropanoic acid (MAMA-SG1) initiators for the 'grafting-from' method to obtain star architecture of poly 4-vinylpyridine (P4VP) from JEFFAMINE®. The structure of macroinitiator was confirmed by amide bond present in NMR and FTIR spectroscopy. Furthermore, the macroinitiator was used to polymerise 4VP. P4VP from JEFFAMINE-SG1 shows a monomodal peak in the SEC chromatogram, indicating more control polymerisation process.

Key words: Nitroxide Mediated Polymerisation, 4-vinylpyridine, star polymer

INTRODUCTION

Nitroxide-mediated polymerisation (NMP) is a powerful tool for the synthesis of macromolecular architectures.[i,ii] NMP is well-documented for the design of new initiators [iii], kinetic investigation [iv,v] and preparation of new materials [vi]. Block [vii,viii] and graft [ix] copolymer as well as star shaped polymers [x-xiii] prepared from NMP indeed show good structural control producing polymers with narrow molar mass distribution at high conversion. The synthetic approaches to star polymers are classified by two methods which are "arm-first" methods and "core-first" methods. The "arm-first" method involves living macromonomers or macroinitiators which link together in the core with vinylic cross linker such as divinylbenzene (DVB).[xiv] On the other hand, the "core-first" methods employs multifunctional initiators that simultaneously initiate the polymerisation of monomers to form the arms of the star polymer.[x]

MAMA-SG1 is an alkoxyamine with high potential nitroxide because it has a high dissociation rate constant and a terminal carboxylic acid group. This functional group allows further modification or transformation processes to open new possibilities for complex molecules that are not accessible with TEMPO nitroxide.[xv] In 2008, Vinas *et al.* reported the preparation of MAMA-SG1 bearing a N-succinimidyl ester group **(1)** (Scheme 1).[xvi] This alkoxyamine initiator can be attached to OH- and NH_2- functional groups, the later used as macroinitiator for block copolymer preparation.[xvi,xvii] Silica nanoparticles were also grafted with activated MAMA-SG1 **(1)** to polymerise styrene from the surface.[xviii]



Scheme 1: Synthetic route to activated MAMA-SG1 with NHS.[xvi]

Star polymers with MAMA-SG1 was explored by Dufils and his co-workers by intermolecular radical addition of alkoxyamine onto olefins.[xix] They synthesised 3- and 4-arms initiators and star polystyrene from this reaction was controllable with dispersity not exceeding 2. Meanwhile, Robin *et al*. synthesised trifunctional alkoxyamine SG1 with 1,3.5-tris(2-hydroxyethyl)-1,3,5-triazine-2,4,6(1H,3H,5H)-tri-one.[xx] Well-defined star polymers of *n*-butyl acrylate (*n*BuA), styrene (S) and block copolymers poly(BuA-*b*-PS) were reported as products from this trialkoxyamine initiator.

In this study, we introduce star macroinitiator with SG1 end functionality using polyetheramine JEFFAMINE® T-403 grafted with NHS activated MAMA-SG1. Then, P4VP was prepared by core first method. The chemical structure were characterised with FTIR and ^{1}H NMR.

RESEARCH METHOD

Materials

All solvents employed were HPLC grade or better and used directly as received unless otherwise stated. Methyl methacrylate, MMA (Aldrich, 99%) and 4-vinylpyridine, 4VP (Aldrich, 95%) were distilled from calcium hydrate before used. 2-({tert-butyl [[1-(diethoxyphosphoryl)-2,2-dimetylpropyl]amino}oxy)-2-methylpropanoic acid (MAMA-SG1) and JEFFAMINE® T-403 were kindly gifted of TU/e, Eindhoven and HUNSTMAN, UK respectively. PPI (polypropylene imine) dendrimers, generations 2, were purchased from SyMO-Chem BV (The Netherlands). 2-(1H-benzotriazol-1-yl)-1,1,3,3-tetramethyluronium hexafluorophosphate (HBTU) and *N*,*N*-Diisopropylethylamine (DIPEA) were purchased from Sigma-Aldrich.

Synthesis of activated alkoxyamine, 2-methyl-2-[N-tert-butyl-N-(1-diethoxyphosphoryl-2,2-dimethylpropyl) aminoxy]-N-propionyloxysuccinimide (MAMA-NHS (1))

This compound was synthesised following a literature procedure.[xvi] MAMA-SG1 (0.5 g, 1.31 mmol) and N-hydroxysuccinimide (NHS) (0.18 g, 1.57 mmol) were dissolved in 2 mL THF and deoxygenated by nitrogen bubbling for 15 minutes. Then, a degassed solution of 0.3 g N,N'-dicyclohexylcarbodiimide (DCC) in 0.5 mL THF was added. After stirring at 0 °C for 1.5 hours, the precipitated N,N'-dicyclohexylurea (DCU) was removed by filtration and washed with a minimum of cool THF. The filtrate volume was reduced under vacuum to one third and kept at -20 °C for 2 hours in order to precipitate the residual DCU. After filtration, the precipitation was performed in pentane. The obtained solid was further washed with water to remove NHS and dried under vacuum. The alkoxyamine was obtained as a white powder. ^{1}H NMR (400 MHz, $CDCl_3$) (ppm): 1.17–1.33 (m, 24H), 1.82 (s, 3H), 1.88 (s, 3H), 2.82 (s, 4H), 3.31 (d, 1H), 3.95–4.35 (m, 4H). Mixture with DCU 2.00-1.15 (m, 8H). ^{31}P NMR (400 MHz, $CDCl_3$) (ppm): 24.89. Yield: 200mg (0.40 mmol).

Synthesis of P4VP from JEFFAMINE functionalise MAMA-SG1

Activated alkoxyamine **(1)** (24 mg, 0.05 mmol) and JEFFAMINE® T-403 (20 mg, 0.045 mmol) were added to a Schenk flask and degassed for 15 minutes by nitrogen bubbling. Then, degassed 0.05 mmol DCC in 2 mL DMF was added and stirred at room temperature for 3 days. The precipitated DCU was removed by filtration. Then, the filtrate solution was precipitated in pentane and dried in vacuum oven overnight. The end product was obtained as a yellow sticky material, grafted JEFFAMINE **[2]**. ^{1}H NMR (400 MHz, $CDCl_3$) (ppm): 0.85 (s, **CH_3**-CH_2- from JEFFAMINE), 1.01-1.36 (m, **-CH_3** from MAMA-SG1), 1.57-1.86 (m, **CH_3**-C-C(O)), 2.61 (m, -N-**CH**-P from MAMA-SG1), 3.3-4.12 (m, **-CH_2-** from JEFFAMINE and MAMA-SG1), 8.14 (s, **NH**(CO)) .

Grafted JEFFAMINE **(2)** (30 mg; 0.02 mmol) and 4VP (1.21 g, 11.5 mmol) was added to a Schlenk flask and immersed in a pre-heated oil bath at 110°C for 24 hours. The reaction was quenched by cooling the mixture in an ice-water bath and the polymer was precipitated in diethyl ether, followed to dry in a vacuum oven overnight. Solid white polymer was obtained. Yield: 500 mg; M_n: 119000 g/mol; PDI: 1.4

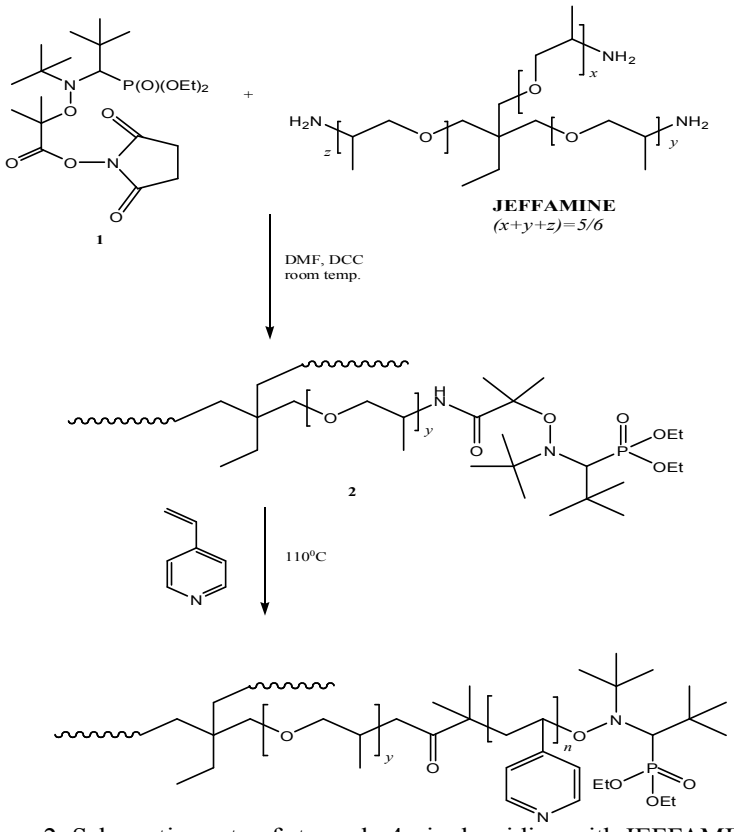
Methods

^{1}H NMR analyses were performed in $CDCl_3$ solution, at 25°C using a Bruker Avance 400 (400 MHz) spectrometer. The chemical shift was calibrated using the solvent peak (δ = 7.26 ppm). The Fourier Transform InfraRed (FTIR) spectroscopy was carried out in the solid state on a Perkin Elmer Spectrum 100. GPC analysis using DMF (0.1 M LiBr) as eluent (elution rate: 1 min/mL) was performed using two PSS GRAM analytical (300 and 100 Å, 10 l) columns on an Agilent 1200 series equipped with a Wyatt Optilab rEX refractive index detector thermostat at 40 °C and a Wyatt DAWN HELEOS-II multi angle light scattering (MALS) detector. Molecular weights and PDI were calculated from the MALS signal using the ASTRA software (Wyatt) and a dn/dc value of 0.225 mL/g (P4VP) [xxi] in DMF. Before analysis, samples were filtered through a 0.45 µm PTFE filter (13 mm, PP housing, Whatman).

RESULT AND DISCUSSION

The synthesis of $sP(4VP)_3$ was carried out according to Scheme 2. It involves (1) functionalisation of MAMA-SG1 with NHS, (2) Grafting the activated alkoxyamine (MAMA-NHS) to JEFFAMINE® and (3) polymerisation.

For MAMA-NHS **(1)**, the reaction of MAMA-SG1 with NHS in the present of N,N'-dicyclohexylcarbodiimide (DCC) was carried out at 0 °C in THF for 1.5 hours. Then, the product was precipitated in pentane as a white powder. The carbonyl band in FTIR spectra shifted from the free acid MAMA-SG1 at 1718 cm^{-1} to the NHS ester 1741 cm^{-1}. The succinimidyl C=O group appears at 1816 and 1781 cm^{-1} (Figure 1a). The FTIR spectrum in Figure 1b shows the new band at 1625 and 1572 cm^{-1} assigned to the amide bond (-CONH-) *i.e.* the C=O stretching and N-H bending vibration band.



Scheme 2: Schematic route of star poly 4-vinylpyridine with JEFFAMINE®

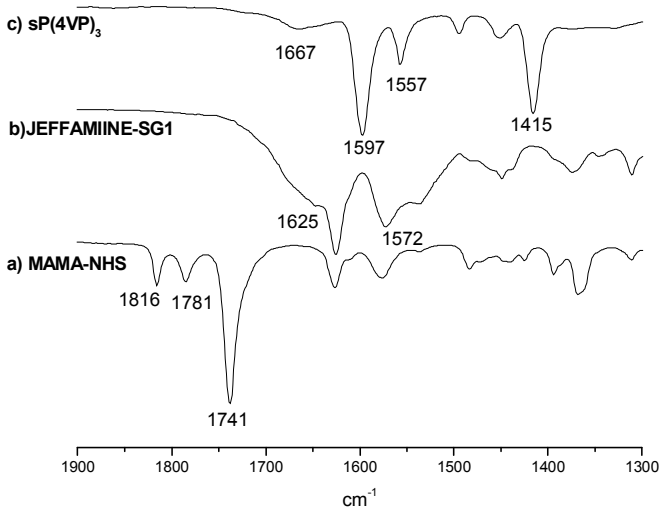


Figure 1: FTIR spectrum of (a) activated alkoxyamine, MAMA-NHS); (b) JEFFAMINE® functionalise SG-1; (c) star polymer 4-vinylpyridine, $sP(4VP)_3$

In addition, ^{1}H NMR confirmed the structure of MAMA-NHS with the peaks of the methyl (**b**, **c**, **e**, **g**), methylene (3.95-4.35 ppm) and –CH (3.31 ppm) from MAMA-SG1 as well as the methylene of the succinimidyl ester appearing at 2.82 ppm (Figure 2a). Then, the activated alkoxyamine was grafted to JEFFAMINE® at room temperature in DMF to form star initiator **(2)** as a yellow sticky material. The ^{1}H NMR spectrum shows characteristic peaks of both the

JEFFAMINE® bands (0.85 ppm for free $-CH_3$, 3.20 – 4.20 ppm for CH and CH_2) and the SG-1 (**b**, **i**, **k**, **m** for $-CH_3$ groups). Moreover, the amide linker can be identified in the spectrum at 8.14 ppm (Figure 2b).

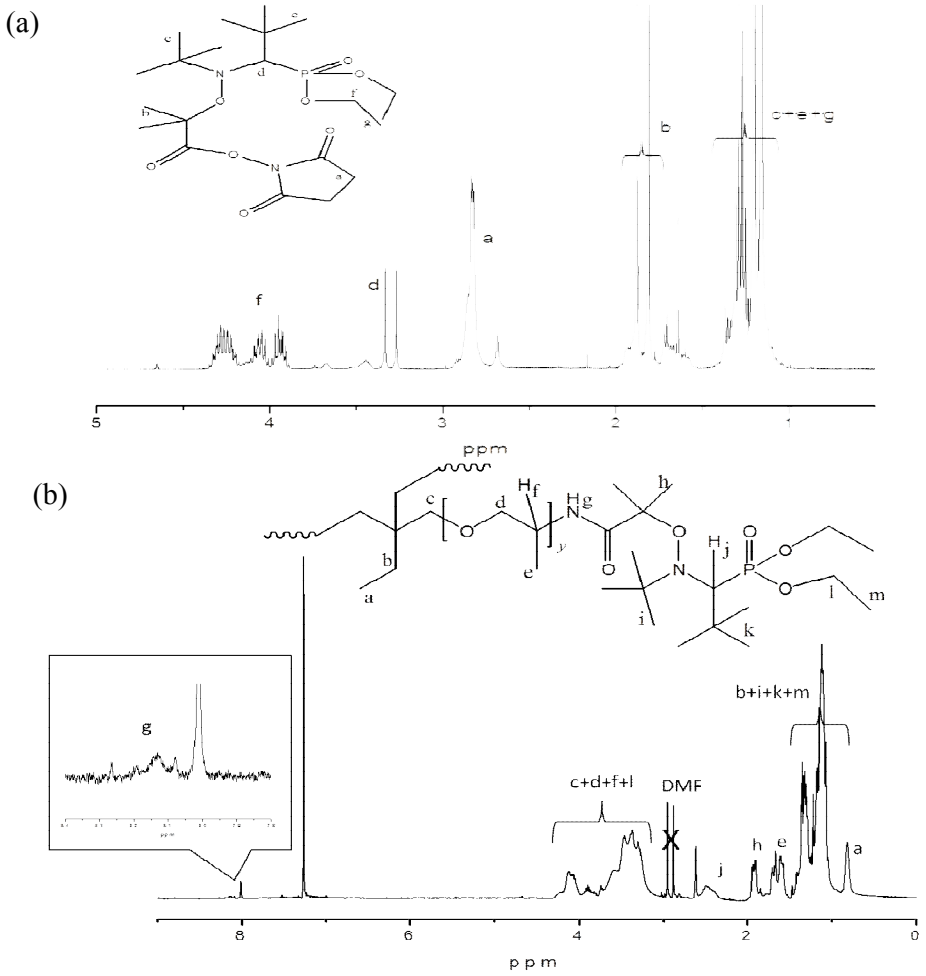


Figure 2: ^{1}H NMR of activated alkoxyamine MAMA-NHS (a) and JEFFAMINE® functionalised with NHS-alkoxyamine (b).

P4VP with the functionalised JEFFAMINE®-SG1 macroinitiator (**2**) was synthesised at 110 °C yielding white polymer product at 98% conversion. Figure 1c shows the position of the amide bond in $sP(4VP)_3$ shifted from 1625 to 1666 cm^{-1} with the presence of P4VP bands at 1597, 1557 and 1451 cm^{-1}. A molecular weight of 170000 g/mol, M_w, measured by SEC equipped with a MALS detector was obtained compare to the M_n theoretical of 106000 g/mol (Figure 3). The SEC chromatogram shows a monomodal peak with a dispersity of 1.4. Termination reaction are never inhibit during NMP leading to disproportionation and combination reactions between radicals. According to Vinas *et al*., the dissociation rate constant (k_{d1}) of C-ON bond homolysis in **(1)** is 5 s^{-1} (E_a = 103 kJ mol^{-1}) which is 15 times higher than MAMA-SG1 (k_{d1} = 0.32s^{-1}. E_a = 112 kJ mol^{-1}).[xvi,[xxii]] The higher k_{d1} value can be ascribe to a long-range polar effect of NHS moiety in the activated MAMA-NHS. Besides that, we also observed a broad tailing at the low

molar mass side of the chromatogram probably due to autopolymerisation of 4VP at high temperature. Baumann and Schmidt observed that the rate of autopolymerisation of 4VP is in order 11%/h at 125 °C.[xxiii] A summary of the experiment is provided in **Error! Not a valid bookmark self-reference.**.

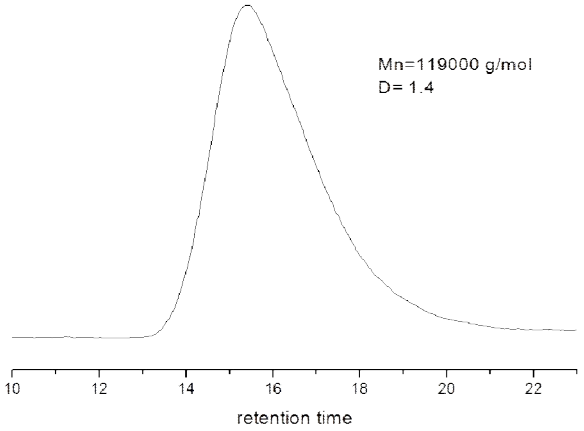


Figure 3: SEC traces (RI signals) of $P(4VP)_3$ with JEFFAMINE® star initiator at a ratio $[M]_0/[I]_0$=370

Table **Error! No text of specified style in document.**.1: Experimental results of star polymerisation of 4-vinylpyridine

Entry	**time, min**	**Conversion [a] (%)**	$M_{n\ theo}$ [b] **g/mol**	$M_{n\ GPC}$ [c] **g/mol**	$M_{w\ MALLS}$ [c] **g/mol**	D [c]
$sP(4VP)_3$ [d]	300	98	106000	119000	170000	1.4

[a] Conversion calculated by ^{1}H NMR through integration of CH_2 peaks of 4VP (5.94 and 5.46 ppm) and P4VP (2.10-1.41 ppm). [b] $M_{n\ theo}$ calculated by ^{1}H NMR, M_n= (molar fraction x $[M]_0/[I]_0$ x M_w monomer) + M_w macroinitiator. [c] Measured by DMF GPC with multi angle light scattering detector (MALS). [d] Experimental condition: $[I]_0/[4VP]_0$ = 1/370 per arms.

CONCLUSION AND SUGGESTION

Multifunctional initiators as the core molecules was synthesised from JEFFAMINE® to obtain 3- arms for the polymerisation of 4VP. This structure of the alkoxyamines was confirmed spectroscopically. $s(P4VP)_3$ was synthesised from the macroinitiator with high molecular weight (~10^5 g/mol). However, low molecular weight products were obtained in the polymerisation either due to autopolymerisation or termination reactions at the early stage of the polymerisation. Further investigation to control the rate of polymerisation and to synthesise well-defined polymer will be necessary to optimise this procedure.

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